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Ammonia based CO_2 capture process using hollow fiber membrane contactors

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ABSTRACT

Due to its low regeneration energy demands relative to MEA, ammonia is one of the most attractive solvents for post-combustion CO_2 capture processes. Nevertheless, additionally to a lower kinetic constant, a high ammonia slip takes place when the absorption process is performed in a packed column. In this study, the feasibility of an ammonia based CO_2 capture process using hollow fiber membrane contactors is investigated. CO_2 absorption experiments in ammonia have been performed with porous polypropylene membranes (Oxyphan) and with two different dense skin composite hollow fibers: tailor made (Teflon AF2400) and commercial (TPX). It is shown that microporous membranes do not offer stable performances, due to salt precipitation and pore blocking. Contrarily however, dense skin membranes show stable and attracting performances, whatever the operating conditions: reduced ammonia slip and intensified CO_2 mass transfer are obtained compared to packed column. The potentialities of dense skin membrane contactors, particularly based on fluorinated polymers, are discussed with regard to both increased CO_2 mass transfer performances and mitigation of ammonia volatilization compared to conventional gas/liquid contactors.

1. Introduction

Climate change, which is closely related to anthropogenic CO_2 emissions, is one of the main growing issues our society has to face. Particularly, electricity production, mostly performed using fossil fuels, is the largest stationary source. Beyond promoting renewable energies, large efforts have been carried out to reduce CO_2 emissions through improved power plant efficiencies. Nevertheless, developing technologies able to remove CO_2 is still required in order to achieve the recommended objectives. Coal being the most widespread resource available, post-combustion CO_2 capture from coal fired-plant flue gas is of higher interest, especially for retrofit purpose [1]. Up to now, the most mature technology for post-combustion capture consists in reacting CO_2 with a chemical solvent in a packed column. The reference solvent is an extremely reactive primary amine with fast reaction kinetics: monoethanolamine (MEA). Despite extensive research efforts, large scale deployment is not likely to happen. Indeed, energy penalty related to MEA based CO_2 capture process in packed column is prohibitive consequently to the high regeneration energy demand induced by this solvent (around 4 GJ per ton of CO_2 removed) [2]. Besides, MEA is corrosive and is subjected to thermal and oxidative degradation by O_2 and SO_2. As a result, volatile pollutants are produced and significant MEA losses take place (up to 6.5 kg MEA per ton CO_2) [3]. Accordingly, an important solvent make up increasing the operational cost and a deep desulfurization of the flue gas (content less than 5 ppm) are compulsory [4].

For these reasons, numerous studies investigate new absorption solvents for post-combustion CO_2 capture and, over time, ammonia in aqueous solution has appeared as a serious candidate for that purpose [5]. Firstly, NH_3 could significantly reduce the energy regeneration demands and save up to 75% energy compared to MEA. In addition, NH_3 is cheaper than MEA (ratio 1/6 on the same mass basis) and its absorption capacity is 3 times higher. Finally, NH_3 is not corrosive and does not suffer from thermal or oxidative degradation. On the contrary, reusable products can be formed when reacting with NO*x* and SO*x* and a combined capture of these pollutants can be introduced. Nevertheless, ammonia shows two main drawbacks that lower its interest. First of all, ammonia absorption kinetics is less favorable than MEA, leading thus to larger absorber which increases the investment cost. Then, being highly volatile, high ammonia losses are generally observed when the absorption is performed in direct gas/liquid units such as packed columns. A washing section is therefore required to meet the ammonia emissions limits, thereby increasing again the

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operating costs. Additionally, a solvent make-up must be considered. In that context, a gas/liquid contactor offering both improved CO_2 mass transfer performances and mitigating the ammonia slip compared to packed column could be of major interest.

Initially tested for CO_2 absorption by NaOH using microporous hollow fibers [6,7], membrane contactors are now considered as one of the most promising intensification strategies [8]. Generally speaking, hollow fiber membrane contactors could logically be of interest as gas/liquid units for the absorption of CO_2 in ammonia solution. Indeed, the very large interfacial area developed by membrane contactors (up to 6000 m^2/m^3) compared to packed columns (around 300 m^2/m^3) could potentially result in a significant improvement of the CO_2 absorption capacity compared to conventional absorption processes [9]. Furthermore, ammonia losses due its high volatility being certainly worsened by a direct contact between gas and liquid, the indirect gas/liquid contact allowed by membrane contactors could possibly lead, at first glance, to ammonia slip mitigation. To our knowledge, no study discussing the feasibility of a process using hollow fiber membrane contactors for CO_2 absorption in ammonia has been reported up to now.

A large number of studies dealing with CO_2 absorption by membrane contactors involve hydrophobic microporous hollow fibers for which impressive intensification factors have been reported [10,11]. Nevertheless, membrane wetting usually takes place after long term use decreasing thus the overall mass transfer coefficient [12]. While many studies have shown that the long term use of MEA for CO_2 absorption results in the membrane wetting for several membrane materials, no study discusses the use of microporous hollow fiber for CO_2 absorption in ammonia. In this work, the potential of microporous hollow fibers as gas/liquid contactor for an ammonia based CO_2 absorption process will be evaluated and discussed.

To avoid membrane wetting, the reference alternative consists in using composite hollow fibers membrane contactor where a thin dense layer added to a microporous support acts as a physical barrier facing the liquid phase [13,14]. In that case, wetting is suppressed while mass transport performances can be found comparable to those observed in microporous membrane contactors [15] in the peculiar case where the dense skin is properly chosen. Composite hollow fiber membrane contactors as gas liquid contactors for ammonia based CO_2 capture process could be of interest compared to conventional CO_2 absorption in a packed column. Indeed, a chemically resistant composite fiber made of a thin dense layer ideally highly permeable to CO_2 but less permeable to NH_3 could potentially lead to a high CO_2 mass transfer intensification while drastically lowering ammonia slip.

In the following, the feasibility, advantages and drawbacks of both conventional microporous and composite hollow fibers for the absorption of CO_2 in ammonia will be discussed on the basis of experimental work performed using different lab scale modules.

Numerous publications have been already reported for membrane contactors fundamental studies and applications [16,17]. Generally speaking, the transfer of a single species is systematically studied, either in an absorption or in a stripping configuration (Fig. 1). The study detailed in this paper is however unique in that the simultaneous transfer of two different reacting compounds (CO_2 and NH_3) in two opposite directions is considered (Fig. 1c). The system is further complicated by the role of water and the possibility to generate precipitating solids through the reaction between CO_2, NH_3 and H_2O. As a consequence, solid salt formation as well as ammonia causticity should absolutely be taken into account for fiber selection.

The objectives of the study are the following:

1. Evaluate the possibilities and limitations of membrane contactors based on microporous membranes for CO_2 absorption in ammonia.
2. Achieve dense materials screening tests, in order to identify the most appropriate dense skin polymer for CO_2 absorption in ammonia, with an emphasis on chemical resistance and precipitating salt complications.
3. Design dense skin composite hollow fiber membrane contactors based on the polymer proposed in step 2, and achieve absorption tests at laboratory scale, with an analysis of the effect of different operating conditions on process performances.
4. Determine the mass transfer characteristics of the different membrane contactors and perform a performances comparison with conventional packed columns.

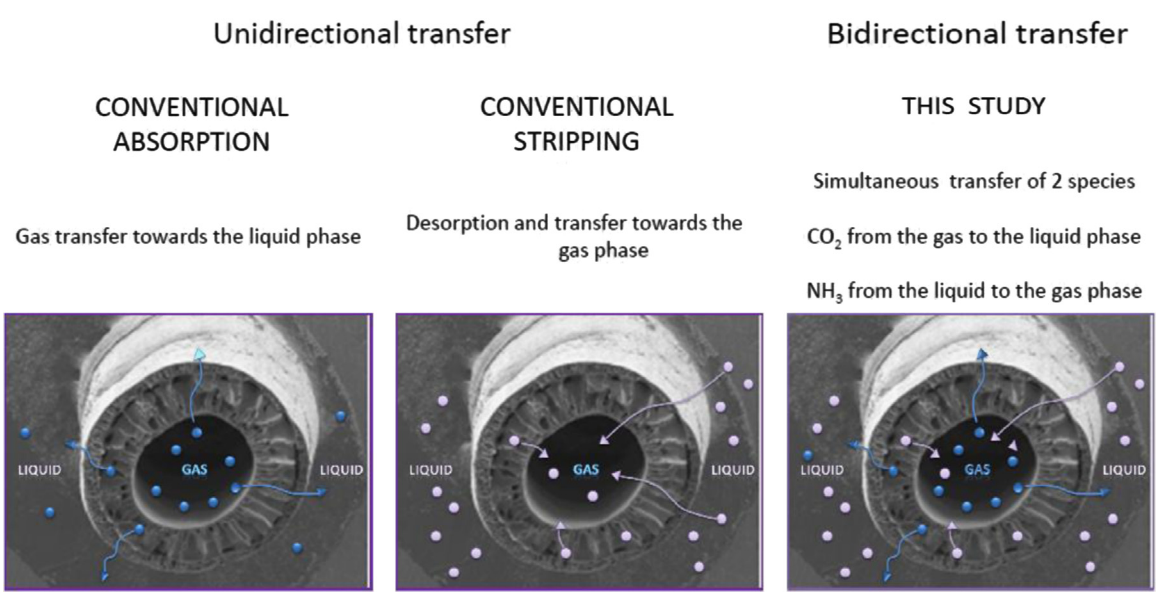

Fig. 1. Different types of situations investigated for gas–liquid membrane contactors applications. Studies almost systematically address a single solute absorption (a) or stripping (b) operation. In this study, the simultaneous CO_2 absorption and NH_3 stripping is considered (c).